

# Effect of $\text{Cd}^{2+}$ on the Growth and Thermal Properties of $\text{K}_2\text{SO}_4$ crystal

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## Abstract

Single crystals of pure and  $\text{Cd}^{2+}$  doped potassium sulfate were grown from aqueous solutions by the slow evaporation technique. From nutrient solutions with a  $\text{CdSO}_4$  concentration of 4 wt.% crystals containing 0.014 wt.% dopant concentration could be obtained. The X-ray diffraction patterns of powdered crystals confirmed their crystal structures for both cases. Thermal analysis of pure crystals shows that the  $\alpha - \beta$  phase transformation peak around  $580^\circ\text{C}$  is superimposed with spurious effects, while for  $\text{Cd}^{2+}$  doped crystals this is not the case. The thermal hysteresis of the phase transition is 8 K for undoped  $\text{K}_2\text{SO}_4$  and is reduced to 3.5 K for  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$ . Compared to undoped crystals, the optical transmittance of  $\text{Cd}^{2+}$  doped crystals is higher.

*Key words:* A. inorganic compounds, B. crystal growth, C. differential scanning calorimetry (DSC), C. thermogravimetric analysis (TGA), D. phase transitions  
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## 1. Introduction

Potassium sulfate  $\text{K}_2\text{SO}_4$  crystallizes at room temperature in the orthorhombic olivine type structure and has four formula units per  $D_{2h}^{16} = Pnma$  unit cell, with lattice constants  $a_0 = 7.476 \text{ \AA}$ ,  $b_0 = 10.071 \text{ \AA}$ , and  $c_0 = 5.763 \text{ \AA}$  [1]. The mineral olivine  $(\text{Mg,Fe})_2\text{SiO}_4$  is a major component of the earth's crust.  $(\text{Mg,Fe})_2\text{SiO}_4$  and its isomorphs  $\text{A}_2\text{BO}_4$  (where  $\text{A} = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$ ,  $\text{B} = \text{S}, \text{Se}$ ) exhibit many interesting physical properties and phase equilibria that were studied repeatedly [2,3,4,5].

Upon heating  $\text{K}_2\text{SO}_4$  undergoes a first order transformation at  $T_t \approx 580^\circ\text{C}$  to a hexagonal structure  $D_{6h}^4 = P6_3/mmc$  with  $a_0 = 5.92 \text{ \AA}$  and  $c_0 = 8.182 \text{ \AA}$  (measured at  $640^\circ\text{C}$  [6]). In this high- $T$  structure the oxygen positions of the  $\text{SO}_4^{2-}$

tetrahedra are only partially occupied as a result of rotational disorder.  $\text{K}_2\text{SO}_4$  crystals that are grown at room temperature from aqueous solution incorporate  $\text{OH}_3^+$  ions. The  $\text{OH}_3^+$  concentration decays in the temperature region from  $300^\circ\text{C}$  to  $450^\circ\text{C}$  and usually crystals are destroyed by this process [6].

El-Kabbany [7] has reported a thermal hysteresis for the solid phase transformation with  $T_t = 571^\circ\text{C}$  at heating and  $T_t = 566^\circ\text{C}$  at cooling. Electrical conductivity measurements on single crystals have been carried out by Choi et al. [8] who found  $T_t = 586.9^\circ\text{C}$  on heating and  $T_t = 581.5^\circ\text{C}$  on cooling, with a thermal hysteresis of 5.4 K. Most of the samples crack near  $500 \pm 30^\circ\text{C}$  and show an abrupt drop in electrical conductivity. The hysteresis phenomena, cracking, and electrical “pretransition phenomena” were attributed to rotational disorder of  $\text{SO}_4^{2-}$  ions [8] and inclusions of  $\text{OH}_3^+$  [6]. The present authors reported recently, that the addition of  $\text{Cd}^{2+}$  to the nutrient solution during  $\text{K}_2\text{SO}_4$  crys-

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tal growth leads to an improvement of the crystalline quality [9]. In this paper, the influence of  $\text{Cd}^{2+}$  on the growth and on thermal and optical properties of  $\text{K}_2\text{SO}_4$  crystal is studied in more detail.

## 2. Experimental

Colorless and transparent crystals of pure potassium sulfate could be obtained by slow evaporation of the solvent from saturated aqueous solutions.  $\text{K}_2\text{SO}_4$  usually crystallized in prismatic crystals, the  $\vec{b}$ -axis was found along the long axis of the prism and the  $\vec{c}$ -axis was along one edge of the quasi-triangular basal plane.  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  and  $\text{K}_2\text{SO}_4:\text{Fe}^{2+}$  crystals were grown by the same method from solutions containing 4 wt.% of  $\text{CdSO}_4$  or  $\text{FeSO}_4$ , respectively. The growth process was performed in a multi-jar crystallizer (Fig 1, top) to ensure identical growth conditions. In a period of 60 days, we were able to grow colorless, transparent  $\text{K}_2\text{SO}_4$  single crystals with well-developed faces having dimensions of  $\sim 2.5 \times 1.5 \times 1 \text{ cm}^3$  as shown in Fig. 1, bottom. Contrary, the growth rate of colorless  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  crystals was much lower: in a period of  $\sim 70$  days crystals up to 3 mm in diameter could be grown.

The crystals were characterized by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), by X-ray powder diffraction, and by simultaneous Differential Thermal Analysis/Thermogravimetry (DTA/TG), as described recently [9]. A NETZSCH STA409CD DTA/TG/QMS (QMS = Quadrupole Mass Spectrometer) system with skimmer coupling of the QMS was used for the simultaneous analysis of gaseous species that are evaporating from the sample during heating [10]. The shape and position of melting peaks was additionally investigated with a DSC/TG sample carrier and Pt/Rh crucibles with lid. The optical transmission was measured in the region 120 – 230 nm (VUV spectrometer made by Laser Centre Hannover/LZH).

## 3. Results and Discussion

For the undoped  $\text{K}_2\text{SO}_4$  crystals only impurities on the ppm level could be found by ICP-OES. If crystal growth was performed from solutions containing 4 wt.%  $\text{CdSO}_4$ , the resulting crystals contained only 0.014 wt.% of the dopant. From a  $\text{K}_2\text{SO}_4$  nutrient solution with 4 wt.%  $\text{FeSO}_4$ , crystals with 0.076 wt.% Fe concentration were harvested. The



Fig. 1. top: Multi-jars crystallizer used for the simultaneous growth of undoped and doped  $\text{K}_2\text{SO}_4$  crystals. bottom: As grown undoped  $\text{K}_2\text{SO}_4$  crystal.

small value of the  $\text{Cd}^{2+}$  distribution coefficient  $k_{\text{Cd}} \approx 0.014/4.0 = 3.5 \times 10^{-3}$  is in agreement with literature data for the system  $\text{K}_2\text{SO}_4\text{--CdSO}_4$  [11] that report an almost vanishing solubility. For iron one calculates a larger distribution coefficient  $k_{\text{Fe}} \approx 0.076/4.0 = 19 \times 10^{-3}$ . But this value is still small, and agrees with Christov's observation [12] that almost pure  $\text{K}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$  are crystallizing from aqueous solutions containing  $\text{Fe}_2(\text{SO}_4)_3$  or  $\text{FeSO}_4$ , respectively. The small values of  $k_{\text{Fe}}$  and especially  $k_{\text{Cd}}$  must lead to high dopant concentrations in the liquid interface layer and slows down the crystallization process, as compared to the growth of undoped crystals.

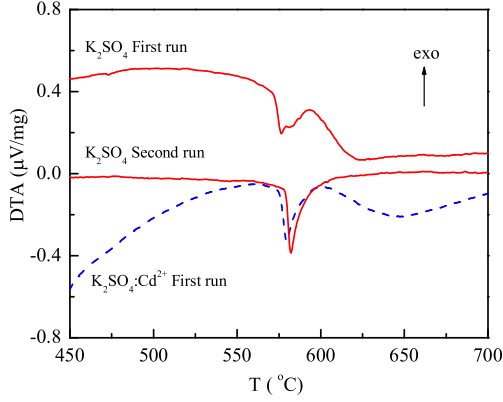
From the X-ray diffraction powder patterns of  $d$ -values and unit cell parameters were calculated with X Powder computer software [13]. The cell parameters that are reported in Table 1 match very well with the standard values for  $\text{K}_2\text{SO}_4$  as found in the literature (PDF card No. 01-070-1488) [1].

Fig. 2 compares results of DTA measurements with heating rates of +10 K/min around  $T_t$  of pure  $\text{K}_2\text{SO}_4$  and of  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  crystals. The curves reveal the expected endothermic peaks around 580 °C related to the phase transition of pure and  $\text{Cd}^{2+}$

Table 1

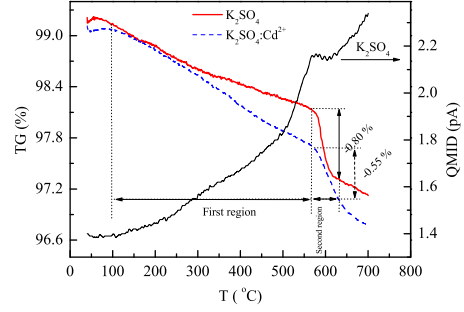
Lattice parameters for pure and doped  $\text{K}_2\text{SO}_4$  crystals.

Crystal	Lattice constants			
	$a_0$ [Å]	$b_0$ [Å]	$c_0$ [Å]	Volume [Å <sup>3</sup> ]
PDF 01-070-1488	7.476	10.071	5.763	433.9
$\text{K}_2\text{SO}_4$	7.489	10.073	5.763	434.7
$\text{K}_2\text{SO}_4:\text{Cd}^{2+}$	7.505	10.064	5.766	435.5
$\text{K}_2\text{SO}_4:\text{Fe}^{2+}$	7.497	10.062	5.767	435.1

Fig. 2. DTA heating run with 10 K/min for  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  crystals.

doped  $\text{K}_2\text{SO}_4$ . In the first heating run of pure  $\text{K}_2\text{SO}_4$  the phase transition peak is superimposed by other effects while in the second heating run the phase transition peak occurs without superimposed features. It will be shown later that traces of water are incorporated in the (formally anhydrous) crystal structure. This water evaporates during the first heating run, and the second heating curve of pure  $\text{K}_2\text{SO}_4$  shows the phase transition peak without additional effects. It is surprising, that  $\text{K}_2\text{SO}_4$  doped with  $\text{Cd}^{2+}$  already in the first heating run did not show the superimposed features. An explanation of this phenomenon can be found using the TG (thermogravimetry) and QMID (Quasi Multiple Ion Detection) curves of  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  crystals that are shown in Fig. 3.

During the TG measurement the gas flowing around the  $\text{K}_2\text{SO}_4$  sample was analyzed by a QMS system with 298 scans for relative mass numbers  $1 \leq m/z \leq 50$  ( $m$  – molecule mass,  $z$  – charge), this means that one mass spectrum is available every 2.5 K. From these mass spectra QMID curves can be calculated that show the ion current for every individual  $m/z$  within the mass detection range given above. Fig. 3 shows such QMID curve for the signal  $m/z = 18$  ( $\text{H}_2\text{O}$ ) of undoped  $\text{K}_2\text{SO}_4$  together with

Fig. 3. Thermogravimetric first heating run for  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  crystals with 10 K/min and QMID for  $m/z = 18$  (water).

the TG curves. The peak around  $T_t$  proves that evaporating water is the origin of the mass loss. The monotonous slope of the QMID background is typical for skimmer QMS coupling systems and plays no role in this discussion.

The TG curves can be divided into two temperature regions: the first one ranges from 100°C up to the onset temperature of the DTA peak ( $T \approx 580^\circ\text{C}$ ) and the second region is around the phase transition ( $580^\circ\text{C} \lesssim T \lesssim 640^\circ\text{C}$ ). In region I the pure crystal loses about  $-1\%$  of its initial mass, while for  $\text{Cd}^{2+}$  doped crystals the mass loss is  $-1.36\%$ . The smaller mass loss of  $\text{K}_2\text{SO}_4$  becomes remarkable for  $T > 300^\circ\text{C}$  where the TG curve for this sample is bent upward.

In region II the mass loss of  $\text{K}_2\text{SO}_4:\text{Cd}^{2+}$  is smaller than the mass loss of pure  $\text{K}_2\text{SO}_4$  by 0.25%. It is obvious, that the small  $\text{Cd}^{2+}$  content encourages the evaporation of water already before the onset of the phase transformation. An explanation if this behaviour cannot be given on the basis of the current data. It should be added here that the influence of the  $> 5$  times larger iron content in  $\text{K}_2\text{SO}_4:\text{Fe}^{2+}$  is just the opposite: Here the TG step at  $T_t$  is larger compared with undoped  $\text{K}_2\text{SO}_4$  (not shown in Fig. 3).

Arnold et al. [6] reported that crystals of  $\text{K}_2\text{SO}_4$  grown at room temperature from aqueous solution incorporate  $\text{OH}_3^+$  ions. They decay in the temperature region from 300°C to 450°C. If  $\text{K}_2\text{SO}_4$  is crystallized above 40°C, the content of water in crystals can be minimized [8,14]. Therefore investigation of the effect of crystal growth temperature in comparison with different concentrations of  $\text{Cd}^{2+}$  on this phenomena of  $\text{K}_2\text{SO}_4$  crystals will be considered in future studies.

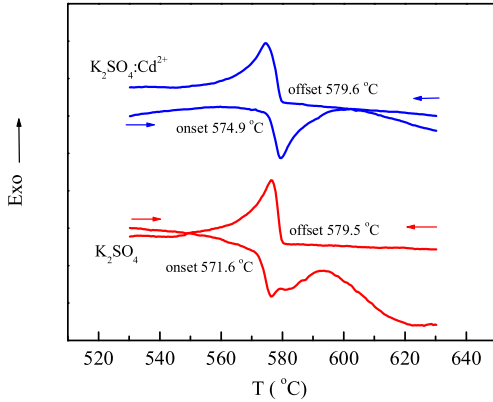


Fig. 4. DTA first heating and cooling curves for  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  and  $\text{K}_2\text{SO}_4$  crystals.

DTA heating and cooling curves around the phase transition peak for  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  crystals are shown in Fig. 4. The transition temperature  $T_t$  can be determined from the intersection of the extended basis line with the tangent at the inflection point (extrapolated onset). It is remarkable that for pure  $\text{K}_2\text{SO}_4$ ,  $T_t$  as obtained from the first heating or cooling runs, respectively, differ considerably by a hysteresis of about 8 K. For  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  this hysteresis is only 4.5 K. It was reported recently that the hysteresis is reduced considerably for both  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  in subsequent (starting from the second) heating/cooling runs [9]. Hence it can be suggested that the effect of  $\text{Cd}^{2+}$  on hysteresis is similar to the effect of annealing for  $\text{K}_2\text{SO}_4$  crystal, if the first heating/cooling run is considered as annealing for the undoped crystal.

Fig. 5 compares the melting behavior of pure  $\text{K}_2\text{SO}_4$  with that of  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  and, for reference, with that of a higher doped  $\text{K}_2\text{SO}_4\text{:Fe}^{2+}$ . For  $\text{K}_2\text{SO}_4$  as well  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  the melting temperature  $T_f = (1068.2 \pm 0.2)^\circ\text{C}$  and the crystallization temperature are almost identical with negligible hysteresis. In contrast, the higher dopant concentration in  $\text{K}_2\text{SO}_4\text{:Fe}^{2+}$  leads to remarkable hysteresis of 0.4 K and shifts the melting point to  $T_f = (1070.4 \pm 0.1)^\circ\text{C}$ . In analogy to Fig. 6 of [9] which represents a model for the  $\beta/\alpha$  phase transformation, an extended two phase region  $\alpha/\text{liquid}$  can explain the shift of  $T_f$  and the hysteresis.

The widths of the  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  melting and crystallization peaks are slightly larger compared to the undoped  $\text{K}_2\text{SO}_4$ , as a result of the minor  $\text{Cd}^{2+}$  dopant concentration. It is remarkable, however, that this impurity leads in the end to improved optical properties.

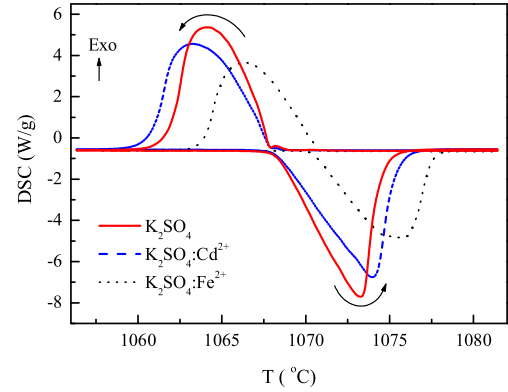


Fig. 5. DSC heating and cooling curves ( $\pm 10$  K/min) near the melting temperature for undoped  $\text{K}_2\text{SO}_4$  and for crystals doped with Cd or Fe, respectively.

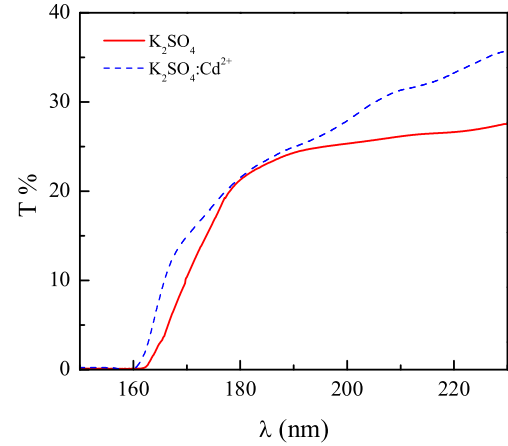


Fig. 6. Optical transmittance  $T$  as a function of wavelength  $\lambda$  for  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  crystals.

Fig. 6 shows that the optical transmission of  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  is higher than the transmission of  $\text{K}_2\text{SO}_4$  for all wavelengths shown here ( $\lambda \leq 230$  nm). This may partially be a result of scattering centers in the crystals that were grown from solutions containing  $\text{Cd}^{2+}$ , as  $\text{Cd}^{2+}$  doped samples can already with the naked eye be recognized to possess a higher optical clarity. Nevertheless it is remarkable that the absorption edge is shifted toward the VUV region, resulting in an increased energy gap of  $\text{K}_2\text{SO}_4\text{:Cd}^{2+}$  compared with undoped  $\text{K}_2\text{SO}_4$ .

#### 4. Conclusion

Pure  $\text{K}_2\text{SO}_4$  and Cd doped  $\text{K}_2\text{SO}_4$  crystals can be grown from aqueous solution by the slow evaporation technique. The incorporation of Cd is weak: From solutions with 4 wt.%  $\text{CdSO}_4$  one obtains

$\text{Cd}^{2+}:\text{K}_2\text{SO}_4$  crystals with only 0.014 wt.% of the dopant. Nevertheless, the influence of cadmium is remarkable: Cd doped crystals contain less water, and the remaining water is loosely bond compared with water in undoped crystals. The optical transparency of  $\text{Cd}^{2+}:\text{K}_2\text{SO}_4$  in the UV region is larger.

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